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^{1}H, ^{19}F AND ^{11}B NUCLEAR MAGNETIC RESONANCE CHARACTERIZATION OF BF_3:AMINE CATALYSTS USED IN THE CURE OF C FIBER-EPOXY PREPREGS*

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Abstract

^{1}H, ^{19}F and ^{11}B nuclear magnetic resonance studies are reported which characterize the complexes of boron trifluoride with monoethylamine and with piperidine, $BF_3:NH_2C_2H_5$ and $BF_3:NHC_5H_{10}$, respectively. These complexes are used as catalysts for the cure of high performance C fiber-epoxy composites from prepregs. The chemical composition of commercial BF_3: amine complexes are variable and contain BF_4^- and $BF_3(OH)^-$ salts together with other unidentified highly reactive species. The BF_3: amine complexes, which are susceptible to hydrolysis, also partially convert to the BF_4^- salt (i.e. $BF_4^-NH_3^+C_2H_5$) upon heating. This salt formation is accelerated in dimethyl sulfoxide solution and in the presence of the epoxides that are present in commercial prepregs. Commercial C fiber-epoxy prepregs are shown to contain either $BF_3:NH_2C_2H_5$ or $BF_3:NHC_5H_{10}$ species together with their BF_4^- salts and a variety of boron-fluorine or carbon-fluorine prepreg species. Considerable variation in the relative quantities of BF_3:amine to it's BF_4^- salt was observed from prepreg lot to lot, which will cause variable viscosity-time-temperature prepreg cure profiles. It is concluded that the chemically stable and mobile BF_4^- salt is the pre-dominant catalytic species, acting as a cationic catalyst for the prepreg cure reactions. During the early stages of cure the BF_3: amine catalyst converts to the BF_4^- salt in the presence of epoxides, whereas the BF_3-prepreg species are susceptible to catalytic deactivation and immobilization.

"Keywords": BF_3:amine catalysts, cure reactions, processing, prepregs.

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1. INTRODUCTION

Diaminodiphenyl sulfone (DDS) cured tetraglycidyl 4,4' diaminodiphenyl methane (TGDDM) epoxies are the most common composite matrices utilized in high performance fibrous composites.

The TGDDM epoxide monomer is a liquid at 23°C, whereas the DDS monomer is a crystalline powder with a m.p. of 162°C. The commercially available prepreg resins such as Narmco 5208**, Fiberite 934 and Hercules 3501, all primarily consist of the TGDDM-DDS epoxy: the latter two systems also contain boron trifluoride catalysts.(1-3)

To manufacture reproducible C fiber-TGDDM-DDS epoxy composites with well-defined lifetimes in service environment requires a knowledge of the parameters that affect composite processing conditions and the resultant structure of the epoxy within the composite. The cure reactions directly control the composite processing and final epoxy network structure. Hence, it is important to understand the cure reactions and the variables that affect such reactions. In previous studies we have reported: (i) systematic Fourier transform infrared spectroscopy (FTIR) studies of the cure reactions of TGDDM-DDS epoxies as a function of cure conditions, DDS concentration and the presence or absence of a BF_3 catalyst(4-7); (ii) the effects of inhomogeneous physical mixing of the TGDDM-DDS components and their degree of chemical purity on the resultant epoxy chemical and physical structure(5,7,8); (iii) the relations between the physical structure, the modes of deformation and failure, and the mechanical properties of TGDDM-DDS epoxies(9,10) and (iv) how specific combinations of moisture, heat and stress affect their physical and mechanical integrity.(9,11-13)

The cure reactions, the viscosity-time-temperature profile, the processing conditions, the resultant epoxy chemical and physical structure, and the mechanical response of a C fiber-TGDDM-DDS cured epoxy composite are modified by the presence of a BF_3-amine complex catalyst within the prepreg. These factors will also be modified by the distribution of the catalyst within the prepreg, its chemical composition and any modification of its structure and activity as a result of exposure to and/or interactions with heat, moisture and the epoxide and amine components within the prepreg.

**Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

The two most common BF_3-amine catalysts used commercially to cure epoxies are boron trifluoride-monoethylamine and boron trifluoride piperidine complexes. Such complexes are latent catalysts at room temperature but enhance epoxide group reactivity at higher temperatures.

In this paper we report ^1H, ^{19}F, and ^{11}B NMR studies of $BF_3:NH_2C_2H_5$ and $BF_3:NHC_5H_{10}$ complexes, with principal emphasis on the former. Our aims were to determine: (i) the chemical composition of commercial BF_3:amine complexes, (ii) their thermal stability in the solid-state and also in solution, (iii) the effect of moisture and heat upon their composition, (iv) the nature of their interaction with the epoxide and amine components utilized in TGDDM-DDS commercial prepregs, (v) the composition of BF_3:amine complexes in commercial prepregs, (vi) their thermal stability in the prepregs and (vii) identification of the chemical structure of the predominant catalytic species of the cure reactions of the prepreg.

2. EXPERIMENTAL

2.1. Materials

The $BF_3:NH_2C_2H_5$ samples investigated were obtained from Alfa, Pfaltz and Bauer, Harshaw and K. and K. Chemical Companys. The C fiber-TGDDM-DDS prepregs investigated were Fiberite 934 and Hercules 3501.

2.2 Experimental

Model compounds and samples of the chemical constituents of the C fiber-TGDDM-DDS prepregs were dissolved in dimethyl sulfoxide (DMSO) and sealed in 5 mm glass tubes suitable for investigation by NMR.

For catalyst studies, solutions were usually in the 0.5-1.0 M concentration range. Prepreg samples were prepared by cutting a 1.0 gm sample of prepreg material into 1/4 inch pieces, removing the backing and placing the remaining 0.79 gms into a vial equiped with an Al foil lined cap. 3 ml of dry DMSO-d6 were added and the sample was agitated on a rotorary stirrer and allowed to stand overnight in order to assure complete solution of the soluble components.

Spectra were obtained on a NT-200 Fourier Transform NMR spectrometer using a super conducting magnet. To observe ^1H, ^{19}F and ^{11}B signals the spectrometer frequencies were 200.071, 188.228 and 64.190 MHz respectively.

3. RESULTS AND DISCUSSION

3.1. Chemical Composition

The chemical composition of the commercial "$BF_3:NH_2C_2H_5$" samples was investigated by ^1H, ^{19}F and ^{11}B NMR.

The ^1H NMR spectrum of $BF_3:NH_2C_2H_5$ should exhibit peaks in three separate regions, namely, the CH_3 region at highest field, the

CH_2 region at an intermediate field and the NH_2 region at lowest field. The theoretical peak intensity distribution should be 3:2:2 for the CH_3, CH_2 and NH_2 regions, respectively. In general the spectra of two components were observed. The major component spectra consisted of a CH_3 triplet (1.090 ppm), a CH_2 quartet (2.612 ppm) and an NH_2 signal (6.156 ppm). The intensity ratios were 3:2:2 respectively and this spectrum was assigned to the $BF_3{:}NH_2C_2H_5$ structure.

A second component was evident in the proton NMR spectra, characterized again by a CH_3 triplet (1.121 ppm), a CH_2 quartet (2.803 ppm) and an NH/OH peak from labile protons (7.27 to 7.63 ppm). Intensity ratios were 3:2: approximately 3. The CH_2 peaks were sharp and showed no indications of additional spin coupling. The spectrum is attributed to (BF_4^- or BF_3OH^-) $NH_3^+C_2H_5$ species. The proton intensity measurements would indicate that BF_4^- is the dominant anion.

The ^{19}F NMR spectra of the commercial "$BF_3{:}NH_2C_2H_5$" samples were investigated. The major components identified in the ^{19}F spectra were $BF_3{:}NH_2C_2H_5$, BF_4^-, and $BF_3(OH)^-$ species and an unidentified highly reactive BF_3 species with an NMR peak in the region of $BF_3(OH)^-$. The $BF_3{:}NH_2C_2H_5$ structure, which was identified by ^1H NMR, is also consistent with observed 1:1:1:1 ^{19}F and 1:3:3:1 ^{11}B NMR quartets where J_{BF}=17.0 Hz. The BF_4^- species was identified by its known chemical shift, together with our independant measurements on $NaBF_4$/DMSO solutions. The $BF_3(OH)^-$ species was identified by (i) its known chemical shift,(14,15) (ii) an observed 1:3:3:1 quartet in the ^{11}B NMR spectrum and (iii) the observation of it's formation from the reaction of $BF_3{:}NH_2C_2H_5$ with H_2O (see later section "Hydrolytic Stability".)

The major ^{19}F environment in the Bauer material shows neither the sharp lines of a symmetrical BF_4^- environment, nor the well resolved 1:1:1:1 quartet patterns of amine:BF_3 adducts. Instead a single broad line (50Hz) is observed in the region of BF_3OH^-. The ^{11}B resonance of this species is also a single broad line. We conclude that an unsymmetrical electronic environment characterizes this species and quadrupole relaxation of ^{11}B occurs. A possible structure is $[(C_2H_5NH_2)_2BF_2^+][BF_4^-]$.

The fluorine species observed in the commercial samples are illustrated in Table 1, in which several other observed ^{19}F NMR peaks are combined under the heading "Miscellaneous".

The chemical composition of a "$BF_3{:}NHC_5H_{10}$" sample was also investigated by ^{19}F NMR. Three fluorine containing environments were found with fluorine distributed as follows, (i) $BF_3{:}NHC_5H_{10}$ (87.3%);

(ii) $BF_4^-NH_2^+C_5H_{10}$ (11.5%) and (iii) $BF_3(OH)^-NH_2^+C_5H_{10}$ (0.2%). Peak assignments were based on our previous investigations of "$BF_3:NH_2C_2H_5$".

3.2. Thermal Stability

Solid "$BF_3:NH_2C_2H_5$" samples that were annealed at 85°C, 115°C or 139°C for 1 hour and then subsequently dissolved in DMSO exhibited no significant dissociation as detected by ^1H. This data is consistent with Harris and Temins(16) observations that BF_3:amine complexes do not dissociate irreversibly to gaseous BF_3 and amine products. (The "BF_3: $NH_2C_2H_5$" was observed to melt near 85°C during these studies.)

However, ^{19}F NMR studies indicate that a small amount of the $BF_3:NH_2C_2H_5$ may slowly convert to BF_4^- and to another species which we do not detect in the ^{19}F spectrum. There is an apparent loss of fluorine as illustrated in Table 2. The small % of $BF_3(OH)^-$ species present in the unannealed sample disappears after a 1 hour anneal at 85°C, presumably as a result of either (i) reaction with species at the glass sample tube surface and/or (ii) formation of species which undergo chemical exchange at an intermediate rate on the NMR time scale.

3.3. Hydrolytic Stability

^{19}F NMR studies of "$BF_3:NH_2C_2H_5$"/DMSO solutions indicated little change occured in the amount of $BF_3:NH_2C_2H_5$, BF_4^- and $BF_3(OH)^-$ species in the presence of added H_2O over a period of 4 days at 23°C.

However, if a large (10 fold) excess of H_2O is added to the "$BF_3:NH_2C_2H_5$"/DMSO solution and the temperatures raised to 85°C for 1 hour, the amount of fluorine present as $BF_3:NH_2C_2H_5$ decreased by ~50% while that present as $BF_3(OH)^-$ $NH_3^+C_2H_5$ increases from 5% to 40%. The more stable BF_4^- species were unaffected by exposure to H_2O at 85°C.

The "$BF_3:NHC_5H_{10}$" species in DMSO behaved similarly to the corresponding "$BF_3:NH_2C_2H_5$" species upon exposure to H_2O at 23°C and 85°C.

3.4. Interaction of "$BF_3:NH_2C_2H_5$" with DDS, and TGDDM

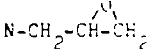
^1H and ^{19}F NMR were utilized to study the interaction of the individual resin components of the C fiber - TGDDM-DDS prepregs with "$BF_3:NH_2C_2H_5$".

It was determined that the ^1H NMR spectrum of DDS in DMSO does not change when $BF_3:NH_2C_2H_5$ is added at ambient temperature. "$BF_3:NH_2C_2H_5$"/DDS/DMSO solutions were then monitored after heating for 1 hour at 85°C, 115°C or 139°C. The broad CH_2 multiplet associated with $BF_3:NH_2C_2H_5$ in the proton spectra decreased with increasing temperature exposure ultimately resulting in a sharp CH_2 quartet which is associated with either $BF_4^-NH_3^+C_2H_5$ or $BF_3(OH)^-NH_3^+C_2H_5$ species. If $BF_3:NH_2C_2H_5$ is heated directly in

DMSO the conversion to BF_4^- and the % fluorine loss is considerably greater than heating $BF_3:NH_2C_2H_5$ in the absence of the solvent, as illustrated in Table 3. The conversion of the $BF_3:NH_2C_2H_5$ to BF_4^- species with associated fluorine loss could preferentially occur at the glass sample tube surface. Hence, such reactions would be accelerated in solution because the mobility of the $BF_3:NH_2C_2H_5$ is enhanced. However, we also cannot rule out the possibility of a reaction between the $BF_3:NH_2C_2H_5$ and the DMSO solvent that enhances conversion to BF_4^- species.

$BF_3:NHC_5H_{10}$ exhibits similar thermal stability trends as $BF_3:NH_2C_2H_5$.

^{19}F NMR studies also indicate that significant changes in the BF_3 species occur upon heating "$BF_3:NH_2C_2H_5$"/DDS/DMSO solutions. The degree of conversion to the BF_4^- salt, for the same thermal exposure, is similar to that observed in "$BF_3:NH_2C_2H_5$"/DMSO solution, Table 3, in the absence of DDS. Hence, we have no direct evidence that DDS competes with $C_2H_5NH_2$ for BF_3 molecules or that DDS enhances BF_4^- salt formation upon heating in DMSO solution.

The ^1H NMR spectra of "$BF_3:NH_2C_2H_5$"/TGDDM/DMSO solutions were investigated as a function of thermal exposure. Heating the solution for 1 hour at 85°C did not produce changes in the ^1H spectra. However, exposures to 115°C or 139°C for 1 hour did produce significant spectral changes. The unmodified TGDDM ^1H NMR spectrum contains two doublets centered at 7.022 and 6.763 ppm which are associated with the two types of aromatic protons. The five different chemical proton environments associated with the  $N-CH_2-\overset{O}{CH-CH_2}$ group result in the series of peaks in the 2.500-3.500 ppm region. We have not attempted to assign peaks in this region to specific proton environments. The essential disappearance of the TGDDM aromatic proton doublets and the modification of the spectral region associated with the TGDDM aliphatic protons after heating for 1 hour at 115°C and 139°C confirms that $BF_3:NH_2C_2H_5$ reacts extensively with the TGDDM epoxide.

^{19}F NMR studies, illustrated in Table 4, indicate that the TGDDM epoxide enhances BF_4^- salt formation in DMSO solution. For example, after exposure to 115°C for 1 hour all the $BF_3:NH_2C_2H_5$ species have disappeared in the presence of TGDDM. However, in DMSO solution in the absence of TGDDM, 50% of the total fluorine species are still in the form of $BF_3:NH_2C_2H_5$ after 1 hour exposure at 115°C, Table 3.

3.5. Catalyst Composition in Prepregs

The catalyst composition in Fiberite 934 and Hercules 3501 prepregs was investigated by ^{19}F

NMR. The epoxy resin in these commercial C fiber-TGDDM-DDS prepregs was dissolved in DMSO.

The fluorine species observed in five different lots of Fiberite 934 were identified and tabulated in Table 5. The catalyst in this prepreg was identified as $BF_3:NH_2C_2H_5$ by ^{19}F NMR. There is considerable varition in the $BF_4^-NH_3^+C_2H_5$ (14.6-60.0%) and the $BF_3:NH_2C_2H_5$ (7.2-48.6%) species from lot to lot.

We assoicate the various additional fluorine peaks observed in the NMR spectra with principally the products of epoxide - active fluorine species reactions. The total fluorine in the form of these products is relatively constant from prepreg lot to lot (28.2-36.3%).

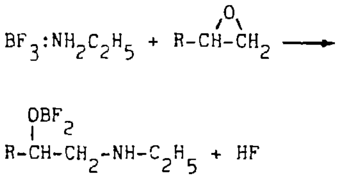
The epoxy resin of a Hercules 3501 sample was dissolved in DMSO and investigated by ^{19}F NMR. The ^{19}F peaks associated with $BF_3:NH_2C_2H_5$ were absent and the 1:1:1:1 quartet associated with $BF_3:NHC_5H_{10}$ was found at an ^{19}F chemical shift value of -155.17 ppm. The fluorine distribution among species found in this sample was $BF_3(OH)^-:NH_2^+C_5H_{10}$ (2.8%); $BF_4^-NH_2^+C_5H_{10}$ (9.9%); $BF_3:NHC_5H_{10}$ (78.3%) and epoxide-fluorine products (9.0%).

The Fiberite 934 prepreg was exposed to a series of temperature-time profiles and the soluble epoxy resin portion dissolved in DMSO and studied by ^{19}F NMR. The ratios of the intensity of the peak associated with $BF_3:NH_2C_2H_5$ (I_{BF_3}) to that intensity of the $BF_4^-NH_3^+C_2H_5$ ($I_{BF_4^-}$) species as a function of exposure conditions are tabulated in Table 6. With increasing anneal temperature the $BF_3:NH_2C_2H_5$ species concentration decreases relative to the $BF_4^-NH_3^+C_2H_5$ species. The presence of steam slows the relative disappearance of the $BF_3:NH_2C_2H_5$ species.

3.6. Catalytic Species and Activity

Our NMR studies indicate $BF_3:NH_2C_2H_5$ is slowly converted to the $BF_4^-NH_3^+C_2H_5$ salt with corresponding loss of fluorine upon heating the solid catalyst. This conversion to the salt is accelerated in DMSO solution and further accelerated in TGDDM/DMSO solutions with an associated 20-30% loss of fluorine upon near complete conversion to the salt. We will now consider the catalytic mechanism and activity of $BF_3:NH_2C_2H_5$ towards the TGDDM-DDS cure reaction in the light of our NMR observations.

The $BF_3:NH_2C_2H_5$ can react directly with an epoxide resulting the formation of a monoboroester and HF.



$$BF_3:NH_2C_2H_5 + R\text{-}CH\text{-}\overset{O}{}\text{-}CH_2 \longrightarrow R\text{-}\underset{}{\overset{OBF_2}{CH}}\text{-}CH_2\text{-}NH\text{-}C_2H_5 + HF \qquad (1)$$

The HF generated then reacts with another $BF_3:NH_2C_2H_5$ to form the salt.

$$BF_3:NH_2C_2H_5 + HF \longrightarrow$$

$$BF_4^-NH_3^+C_2H_5 \qquad (2)$$

The HF can also react with the components of the prepreg resulting in a variety of C-F containing species. The formation of the BF_4^- salt requires two $BF_3:NH_2C_2H_5$ molecules to be in close proximity. Hence, the formation of the BF_4^- salt will intimately depend on the dispersion of the small quantity (0.4 wt %) of the $BF_3:NH_2C_2H_5$ catalyst within the prepreg and, therefore, as such could be highly variable. The monoboroester can act as a catalyst for the cure reactions$^{(17)}$ but is susceptible to deactivation and, also, hydrolysis.

There are reports in the literature of H_2O deactivating the catalytic activity of $BF_3:NH_2C_2H_5$.$^{(18,19)}$ Our NMR studies indicate that $BF_3:NH_2C_2H_5$ can hydrolyze to form the hydroxy fluoroborate salt, particularly at more extreme conditions (i.e. 85°C).

However, our differential scanning calorimetry (DSC) studies$^{(20)}$ indicate that when the $BF_3(OH)^-NH_3^+C_2H_5$ salt is substituted for $BF_3:NH_2C_2H_5$ in a TGDDM/DDS prepreg mix the cure reactions are not modified. This suggests that the $BF_3(OH)^-NH_3^+C_2H_5$ dehydrates back to $BF_3:NH_2C_2H_5$ during the early stages of cure. If, however, a TGDDM/DDS/$BF_3:NH_2C_2H_5$ prepreg is directly exposed to H_2O vapor at 85°C, DSC studies do indicate$^{(20)}$ either (i) a catalytic species is poisoned (probably the monofluoroborate) and/or (ii) the $BF_3:NH_2C_2H_5$ catalyst is leached out of the prepreg.

All BF_3 and BF_3-prepregs species, with the exception of the $BF_4^-NH_3^+C_2H_5$ salt, are susceptible to transformation to less active or non-active catalytic species. Furthermore, our NMR results indicate that the $BF_4^-NH_3^+C_2H_5$ salt does not irreversibly, chemically react with the prepreg components.

For each epoxide group to be catalyzed by a BF_3 species in a prepreg containing 0.4 wt % "$BF_3:NH_2C_2H_5$" catalyst requires each catalytic species to act as a catalyst to ~200 epoxide groups. This means each BF_3 catalytic species has to be chemically stable and mobile. Hence, we suggest that the $BF_4^-NH_3^+C_2H_5$ salt is the predominant catalytic species for the prepreg cure reactions, with the more active BF_3 species becoming deactivated and/or immobilized during the early stages of cure. Harris and Temin$^{(22)}$ have reported that BF_3:amine complexes and their corresponding BF_4^- salts cure epoxides in the same temperature range and cure times. This observation is consistent with the BF_4^- salt being the predominant catalytic species and the BF_3:amine complex coverting to the BF_4^- salt in the presence of epoxide groups. Our DSC studies of the cure reactions of a typical TGDDM/DDS/"BF_3:$NH_2C_2H_5$" *commercial* prepreg containg 0.4 wt% "BF_3:$NH_2C_2H_5$" confirm that the $BF_4^-NH_3^+C_2H_5$ salt is the predominant catalytic species.(20) These studies indicate that the cure reactions occur (i) 50% by $BF_4^-NH_3^+C_2H_5$ cationic catalyzed reactions, (ii) 25% by BF_3:$NH_2C_2H_5$ catalyzed reactions and (III) 25% by non- catalyzed reactions.

4. CONCLUSIONS

^1H, ^{19}F and ^{11}B NMR studies indicate that the chemical composition of commercial "BF_3:$NH_2C_2H_5$" and "BF_3:NHC_5H_{10}" samples are variable and contain BF_4^- and $BF_3(OH)^-$ salts together with another unidentified highly reactive species believed to be $[(C_2H_5NH_2)_2BF_2^+][BF_4^-]$.

At 85°C and above, solid BF_3:$NH_2C_2H_5$ slowly converts to the $BF_4^-NH_3^+C_2H_5$ salt with associated fluorine loss. This salt formation is accelerated in DMSO solution, and further accelerated in the presence of the TGDDM epoxide. There is no evidence the prepreg DDS amine curing agent interacts chemically with the BF_3:$NH_2C_2H_5$.

In the presence of H_2O, BF_3:$NH_2C_2H_5$ readily hydrolyses to $BF_3(OH)^-NH_3^+C_2H_5$ at 85°C. At ambient conditions, however, this hydrolyses is slow with little detectable reaction occuring after 4 days.

In commercial TGDDM-DDS-C fiber 934 and 3501 prepregs "BF_3:$NH_2C_2H_5$" and "BF_3:NHC_5H_{10}" were respectively identified as the prepreg catalytic species. These catalytic species were in the form of the BF_3:amine complex, its BF_4^- salt and a variety of boron-fluorine-prepreg species. The quantities of the BF_3:$NH_2C_2H_5$ and $BF_4^-NH_3^+C_2H_5$ species relative to the total fluorine in the prepreg varied considerably from prepreg lot to lot, i.e. BF_3:$NH_2C_2H_5$ (7-49% range) and $BF_4^-NH_3^+C_2H_5$ (15-60% range). Upon heating the prepreg the BF_3:$NH_2C_2H_5$ is converted to the $BF_4^-NH_3^+C_2H_5$ salt with associated loss of fluorine.

The chemically stable and mobile $BF_4^-NH_3^+C_2H_5$ salt is identified as the predominant catalytic species and acts as a cationic catalyst for the prepreg cure reactions. The more reactive BF_3-amine and - prepreg species are susceptible to conversion to other species with possible catalytic deactivation and immobilization during the early stages of cure.

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6. BIOGRAPHIES

Jim Happe obtained his degrees in chemistry from Iowa State University and the University of Minnesota. He spent five years at the Naval Ordnance Test Station, China Lake, California before coming to LLNL. At China Lake he worked in the area of physical/inorganic chemistry. Since coming to LLNL in 1960 he has been primarily associated with applications of nuclear magnetic resonance to a variety of problems in the areas of physical, inorganic, organic and biomedical chemistry.

Roger J. Morgan is a chemist in the Chemistry and Materials Science Department at Lawrence Livermore National Laboratory, where he investigates the chemical and physical structure, modes of deformation and failure, and mechanical response of polymers and composites, as well as the effect on fabrication and environment on these factors. Before joining LLNL in 1978 he was with McDonnell Douglas Research Laboratories, where he was involved in similar studies. He received his B.S. in chemistry from London University (1965) and his Ph.D., in polymer physics from Manchester University (1968).

Connie Walkup is a Scientific Associate in the Chemistry and Materials Science Department of Lawrence Livermore National Laboratory. His current responsibility is the selection and characterization of epoxy resins used as matrices in fibrous composites. Prior to joining LLNL in 1972, he was a Senion Polymer Technician at Shell Development Company where he was involved with the application of epoxy-based-polymers to adhesives, coatings and composites technologies.

Table 1. Fluorine Species in "$BF_3:NH_2C_2H_5$" from ^{19}F NMR.

Source	% of Total Fluorine as				
	$BF_3:NH_2C_2H_5$	BF_4^-	$BF_3(OH)^-$	Reactive BF_3	Miscellaneous
Alfa	92.5	2.5	2.9	2.0	0.1
Bauer	1.9	15.3	12.4	57.3	13.1
Harshaw	89.7	8.9	0.9	--	0.5
K and K	78.1	11.1	3.1	4.8	2.9

Table 2. Effect of Thermal Annealing on the Fluorine Species in "$BF_3:NH_2C_2H_5$" from ^{19}F NMR.

Anneal Conditions	% Total Original Fluorine as			
	Fluorine Loss	$BF_3(OH)^-$	BF_4^-	$BF_3:NH_2C_2H_5$
Original, unannealed Solid	0	6.1	1.6	92.3
1 hr, 85°C	8.1	0	11.8	80.1
1 hr, 115°C	2.7	0	13.8	83.5
1 hr, 140°C	9.7	0	13.7	76.6

Table 3. *Effect of Heating on the Fluorine Species in* $BF_3:NH_2C_2H_5$/DMSO Solution from ^{19}F NMR.

Heat Conditions	% Total Original Fluorine as			
	Fluorine Loss	$BF_3(OH)^-$	BF_4^-	$BF_3:NH_2C_2H_5$
Unheated Solution	0	6.1	1.6	92.3
1 hr, 85°C	5.1	0	13.1	81.8
1 hr, 115°C	12.9	0	34.7	52.4
1 hr, 140°C	27.3	0	60.2	12.5

Table 4. Effect of Heating on the Fluorine Species in "$BF_3:NH_2C_2H_5$"/ TGDDM/DMSO Solution from ^{19}F NMR.

Heat Conditions	% Total Original Fluorine as			
	Fluorine Loss	$BF_3(OH)^-$	BF_4^-	$BF_3:NH_2C_2H_5$
Unheated Solution	0	6.1	1.6	92.3
1 hr, 85°C	19.4	0	17.8	62.8
1 hr, 115°C	23.0	0	77.0	0
1 hr, 140°C	20.6	0	79.4	0

Table 5. Fluorine Species in Fiberite 934 Lots

	% of Total Fluorine as			
	$BF_3(OH)^-NH_3^+C_2H_5$	$BF_4^-NH_3^+C_2H_5$	$BF_3:NH_2C_2H_5$	Epoxide-BF_3 Products
C2-709	3.8	38.8	25.2	32.2
C3-218	4.6	60.0	7.2	28.2
C3-389	0.5	14.6	48.6	36.3
C3-397	1.5	44.4	22.4	31.7
C3-546	1.4	49.1	18.2	31.3

Table 6. The Effect of Temperature, Time and H_2O on the Relative Extractable $BF_3:NH_2C_2H_5$ and $BF_4^-NH_3^+C_2H_5$ Species in Fiberite 934.

Exposure Conditions	$I_{BF_3}\ I_{BF_4^-}$
Ambient	0.718 ; 0.748
50°C; 1 hr	0.539
50°C; 5 hr	0.554
75°C; 1 hr	0.494
100°C; 1 hr	0.146
100°C; 1 hr + steam	0.326